NEW STRATEGY TO DECOMPOSE NITROGEN OXIDES FROM REGENERABLE FLUE GAS CLEANUP PROCESSES

James T. Yeh, James M. Ekmann, Henry W. Pennline, and Charles J. Drummond

U.S. Department of Energy Pittsburgh Energy Technology Center Pittsburgh, Pennsylvania 15236

INTRODUCTION

Nitrogen oxides (NO $_{\rm X}$) emitted from stationary combustion sources have been identified as important precursors of acid rain formation. Nitric oxide is a precursor to the formation of nitrogen dioxide and is an active compound in photochemical smog formation as well. It initiates reactions in which the products are air pollutants. Consequently, the control of NO emissions is an important factor in reducing air pollution. Well over 90 percent of all the man-made nitrogen oxides that enter the atmosphere are produced by the combustion of various fuels. On a nationwide basis, about one-half of the NO $_{\rm X}$ is from stationary sources.

Two sources of nitrogen contribute to the formation of oxides of nitrogen in the combustion reaction: molecular nitrogen from the combustion air and bound nitrogen from the fuel. Two ways exist to reduce the quantity of NO_{x} dispersed into the atmosphere. One method is control over the combustion reaction that produces the pollutant (combustion modification). Recent experience with combustion modification techniques for coal combustion indicate that NO_{x} emissions for combustion when $\mathrm{low-NO}_{x}$ burners are used can be 50%-60% lower than when employing conventional burners under otherwise identical conditions [1]. Similarly, NO_{x} reductions approaching 70% have been reported in pilot-scale reburning studies [2]. The second method is to remove the pollutant downstream after it is formed (postcombustion cleanup). Postcombustion techniques, which tend to be more complex and expensive, may be necessary when high levels (>70%) of NO_{x} reduction are required or when installing new facilities for which both NO_{x} and SO_{x} controls are mandated.

In certain regenerable, postcombustion cleanup processes, such as the NOXSO process [3], a sorbent is used to remove the $NO_{\rm X}$ from the flue gas. In the regeneration step, a concentrated stream of $NO_{\rm X}$ is produced. This stream would be "recycled" as part of the combustion air back to the coal combustor, where a portion of the $NO_{\rm X}$ would be destroyed. Theoretically, the $NO_{\rm X}$ returned to the coal combustor would cause little change in the concentration of $NO_{\rm X}$ in the exiting flue gas. Thermodynamic equilibrium calculations for $NO_{\rm X}$ formation from combustion indicate that $NO_{\rm X}$ injected into the flame zone of a combustor would be destroyed to a large extent. The formation of $NO_{\rm X}$ and its destruction in practical systems are kinetically controlled, and final concentrations of $NO_{\rm X}$ in flue gas substantially exceed equilibrium values. To assess the extent of the reduction of recycled $NO_{\rm X}$, experimental tests in practical systems are required.

Simulated NO $_{\rm X}$ recycle tests were recently conducted at the Pittsburgh Energy Technology Center (PETC), U.S. Department of Energy, with excellent results [3]. However, the NO $_{\rm X}$ -recycle technique needs improvement if steady-state removal of 90% of the NO $_{\rm X}$ produced from the combustor is required. This paper reports experimental results for two new techniques to improve the destruction of externally injected NO $_{\rm X}$ into a combustor. The first technique involves doping the NO $_{\rm X}$ gas stream to the combustor with methane (other reductants might also be effective). The second technique is injecting the recycled NO $_{\rm X}$ stream at the optimum location (with and without methane doping) for maximum reduction. Test data showed 100% reduction of injected NO $_{\rm X}$ is possible with this technique. A third approach is proposed using a low-NO $_{\rm X}$ burner in combination with the NO $_{\rm X}$ recycle technique to achieve a steady-state 90% NO $_{\rm X}$ removal in the flue gas. The projected results of the third process scheme are based on material balance computations and reasonable expectations of the performance of each component of the process.

THEORETICAL BACKGROUND

The NO_X control techniques described above are based on concepts utilized in other in-furnace NO_X reduction processes. The techniques involve kinetically controlled reduction of NO_X based in part on increased residence time at high temperatures and in part on the presence of chemical species that reduce the NO_X to N_2 , particularly doping the externally added NO_X with methane (CH $_X$). Doping recycled NO_X with a fuel may appear similar to the reburning technique, a term coined by Wendt et al. [4] to describe the process of NO_X reduction by injection of a secondary fuel stream to create a large fuel-rich zone in the combustor. The approach described in this paper, tentatively called "hydrocarbon doping," differs from reburning in that small amounts of secondary fuel are used (approximately 20% of that used in reburning for effective control), and no downstream injection ports are required.

Thermodynamic Equilibrium

The thermodynamic feasibility of in-furnace NO_X reduction was studied using the PETC Multi-Phase Thermodynamic Equilibrium computer code and Sandia National Laboratory's CHEMKIN computer code. Results of the thermodynamic study show the equilibrium concentration of NO at various flame temperatures (see Figure 1). The thermodynamic model simulates pulverized-coal combustion at 20% excess air. Injection of additional NO (referred to as recycle ratio, expressed as the ratio of moles of NO injected to moles of NO formed in the combustion process) was studied at levels of 0%, 90%, and 100%. The calculated data show that at NO recycle ratios as high as 1, virtually no net increase of NO occurs. However, although thermodynamics indicates nearly total destruction of injected NO is feasible (up to a recycle ratio equal to 1), chemical kinetics reaction rates will dictate the final product mix. At a NO recycle ratio equal to 4, the CHEMKIN equilibrium code predicts a 1.8% increase in NO concentration compared to the case with no recycle.

Hydrocarbon Doping

The global reactions involved in doping the injected NO_X with CH, for NO_X reduction are believed to be as follows:

$$CH_4 + 4 NO_2 + 4NO + CO_2 + 2 H_2O$$
 (1)

and

$$CH_4 + 4NO + 2N_2 + CO_2 + 2H_2O$$
 (2)

However, these reactions compete with the methane combustion reaction:

$$CH_{+} + 2 O_{2} \rightarrow CO_{2} + 2 H_{2}O$$
 (3)

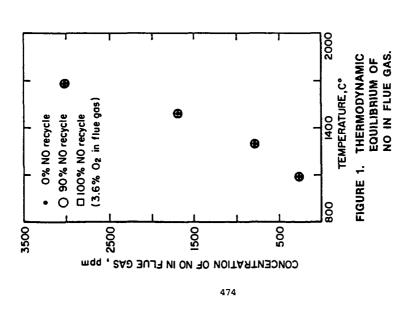
Figure 2 (taken from Chen et al. [5]) describes the chemical mechanism for NO_X destruction by hydrocarbons. The key steps include initial NO destruction by reaction with the methylidyne radical (CH) to form HCN. Subsequent reactions lead to ammonia (or $NH_{\mbox{\scriptsize I}}$ radicals) and eventually to the formation of N_2 .

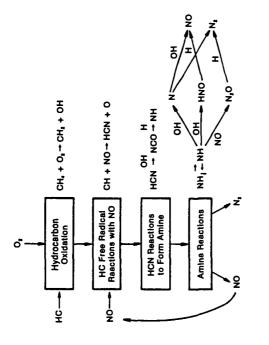
EXPERIMENTAL APPROACH

Test Facilities

The experimental work was conducted at PETC using a tunnel furnace and a 227-kg/hr pulverized-coal combustor. The tunnel furnace is a hot-walled, refractory-lined box with dimensions of 0.97 x 0.97 x 2.80 m and has a single burner in the front wall (interchangeable). It was designed to burn gas, coal-water slurry, or pulverized fuels. Combustion air can be preheated to 400°C (750°F). The burner is supplied with separate flows of combustion air, atomizing air, center-fire air, and natural gas (separate ring). The typical firing rate for the coal-water-mixture is approximately 0.5 x 10^6 W (1.7 MMBtu/hr).

The 227-kg/h (500-lb/h) pulverized-coal combustion test facility is shown schematically in Figure 3. The furnace walls are refractory-lined and water-cooled. The unit is 2.13-m (7-ft)-wide, 1.52-m (5-ft)-deep, and 3.66-m (12-ft)-high, and has a volumetric heat liberation rate of about 165,662 $\mbox{W/m}^3$ (16,000 Btu/hr-ft³) at a thermal input of 1.9 x 10 6 W (6.5 MMBtu/h). The flue gas flow rate is approximately 0.613 cubic meters per second at standard conditions (1300 scfm) (standard condition is 1 atm and 0°C). Coal is charged to the hopper, pulverized to a size consist of 70% minus-200 mesh, and then conveyed by the primary air into a recycle coal loop, where intimate mixing of coal and air occurs. Four adjustable exit tubes are connected to the recycle loop; these convey the primary air-coal mixtures to each of the four burners. It should be noted that the primary air swirl inducer is no longer being used. Secondary air at 315°C (600°F) is fed through swirl vanes surrounding each burner. The flue gas exits the furnace at about 1090°C (2000°F) and passes through a convective heat transfer section and an air preheater.





REACTION MECHANISM FOR NOX DESTRUCTION BY HYDROCARBONS. FIGURE 2.

No./8116

Test Procedure

To simulate the recycle of NO_{X} from a regenerable NO_{X} control process, nitric oxide (NO) from a compressed-gas cylinder was injected into the combustor through the burner(s). Initial NO_{X} concentration at the exit of the combustor was recorded. Nitric oxide gas was then injected into the burner. The NO_{X} concentration in the exiting flue gas reached a steady-state level. In the case of the 227-kg/h pulverized-coal combustor, the point of NO_{X} injection into the burner could be varied. Also, natural gas could be added to the NO_{X} stream. The burner used in the 227-kg/h combustor is shown in Figure 4.

RESULTS AND DISCUSSION

The test results of in-furnace reduction of recycle NO_X with and without assistance from hydrocarbon doping are given in Tables 1 and 2. Table 1 results were obtained from the tunnel furnace tests while burning natural gas and while burning coal-water mixtures. Table 2 contains test results obtained from the 227-kg/h pulverized-coal combustor. The initial NO_X concentration is defined as the NO_X concentration in the furnace exit without any NO injection into the furnace (base line). The final NO_X concentration is that in the exiting furnace flue gas during injection of NO at steady-state conditions. The net NO_X increase is the difference between the concentrations during NO injection and the base-line condition. The reduction of recycled NO_X is the difference between the calculated final NO_X (assuming no in-furnace reduction) and the final NO_X concentration, divided by the difference between the calculated final NO_X concentration. A discussion of the results from the two test series follows.

Tunnel Furnace

Simulated NO $_{\rm X}$ recycle tests were conducted by injecting nitric oxide (NO) into the combustion air stream. The pure NO was delivered from a compressed-gas cylinder. The NO was diluted by the air stream before entering the furnace.

The recycled NO_{X} reductions were in the range of 59% to 79%. The data show a nearly linear relationship between NO_{X} recycle ratio and NO_{X} reduction in moles per minute. This indicates that the higher the NO_{X} concentration in the furnace, the more NO_{X} that is being decomposed. The linear relationship perhaps indicates the decomposition of NO_{X} is a first-order kinetics reaction. Since the reduction of NO_{X} returned to the furnace is not complete, thermodynamic equilibrium among all the reactions species is not being reached within the furnace.

Pulverized-Coal Combustor

Several parameters were studied during this series of tests. The objective was to maximize the reduction of $NO_{\rm x}$ injected into the combustor.

Table 1. In-Furnace Reduction of Recycled ${\sf NO}_{\rm X}$, Tunnel Furnace Tests

				Test No.			
	-	2	3	7	5	9	7
Fuel Type		natural gas			coal-water slurry	er slurry	
Initial NO _x , ppm	31	31	31	510	510	510	510
Final NO _x , ppm	80	134	51	580	946	720	840
NO _x recycle ratio	6.3	12.0	3.0	9.0	0.3	1.0	2.0
Calculated final NO _X , ppm, if in-furnace reduction efficiency = 0	227	403	124	816	663	1020	1530
Net NO _x increase, ppm	611	103	20	70	36	210	330
Reduction of recycled NO _x , \$	75	72.3	78.5	77.0	0.97	93.0	0.89
$NO_{\rm X}$ reduction, 10^{-3} mol/min	0.061	0.13	0.03	0.2	0.1	0.26	9.0

476

Table 2. In-Furnace Reduction of Recycled MO_X, 227 kg/h Coal Combustor Tests

	Test No.					
	8	9	10		12	13
Initial NO _x , ppm	700	700	700	550	550	550
Final NO _X , ppm	770	910	980	980	740	750
NO _K recycle ratio	1.48	1.47	1.47	1.90	1.87	1.77
Calculated final NO _H , ppm, if in-furnace reduction = 0	1739	1731	1731	1596	1579	1523
Net NO _x increase, ppm	70	210	280	430	190	200
Reduction of recycled NO _X , \$	93.3	79.6	72.8	58.9	81.5	79.4
No, of burners used for NO _x injection	2	2	2	4	4	4
Location of NO _x entering into burners	auxilisrý	gas line	primary air	seco.	ndary ir	primary air
NO _x reduction, 10 ⁻³ mol/min	2.85	2.44	2.23	1,90	2.58	2.38
mol CK4/mol NO _x reduced	10.1	0	0	0	14.9	o
CH, to coai eaiorie ratio	0.107]		0.135	

Table 2 (continued). In-Furnace Reduction of Recycled $\mbox{MO}_{R}, \\ 227 \mbox{ kg/h Coal Combustor Tests}$

3 °			Test I	Vo.		
	14	15_	16	17_	18	
lnitiai NO _X , ppm	550	480	510	510	490	490
Final NO _x , ppm	650	685	590	570	490	490
NO _x recycle ratio	1.77	2.04	1.92	1.92	2.05	2.05
Calculated final NO _X , ppm, if in-furnace reduction = 0	1523	1460	1490	1490	1492	1492
Reduction of recycled NO _x , \$	89.7	79.1	91.8	93.9	100	100
No. of burners used for $NO_{\mathbf{X}}$ injection	4	ą	4	5	2	2
Location of NO _x entering into burners		primary air		auxiliary	gms line	primary air
NO _x reduction, 10 ⁻¹ mol/min	2.68	2.37	2.75	2.81	3.1	3.1
mol CH _b /mol NO _X reduced	12.5	0	4.4	0	3.9	3.9
CH. to coai calorie ratio	-0.118	_	0.043		0.043	0.043

The approaches evaluated included variation of the ${\rm NO}_{\rm X}$ injection location in the burner and the use of hydrocarbon doping of the ${\rm NO}_{\rm X}$ stream.

The $NO_{\rm X}$ can be injected into the burner and then subsequently into the combustor by three possible routes: (1) with the secondary air (this represents about 80% of total combustion air), (2) with the primary air and coal stream, or (3) through the auxiliary gas lines (see Figure 4). Four wall-mounted burners are at two different vertical elevations. The $NO_{\rm X}$ may be injected through all four burners or just through the two lower burners.

The location of the injection of $NO_{\mathbf{X}}$ within the burner is important. The data indicate that the extent of NO_X reduction varies in a manner consistent with other kinetically based NO_X reduction schemes, such as air staging or reburning. It is reasonable to assume that the concentration of NO_{x} would be lower at the exit of the furnace if the NO_{x} is injected into the combustor in a more concentrated form. A comparison of $NO_{\mathbf{X}}$ reduction efficiency can be made when the NO_{χ} is injected with the secondary air (test 11) and with the primary air (tests 13 and 15). Tests 13 and 15 show a greater ${\rm NO_X}$ reduction efficiency because the primary air carried the ${\rm NO_X}$ into the combustor at a higher concentration than did the secondary air. The flow rate of secondary air is about four times that of the primary air. The NO_{x} reduction efficiency would be expected to be higher if the NO_{x} is injected into the combustor through the auxiliary gas line (tests 9 and 17) rather than through the primary air line (test 10). By use of the auxiliary gas line to inject the NOx, no other gas is there to dilute the pure NO delivered from the gas cylinder. The highest NO_X reduction efficiency obtained was when the NO_X was injected into the furnace through the auxiliary gas line. injected NO_X . This line. Test 17 showed a 93.9% reduction of the externally This is a very substantial improvement over the previously reported results obtained in the same furnace [3].

Methane doping of the NO_X stream, especially when the NO_X is concentrated, is believed to cause reburning reactions leading to NO_X reduction, as shown in Equations (1) and (2) and in Figure 2. The data indicate that the addition of a small amount of methane to the NO_X stream greatly improves the in-furnace NO_X reduction efficiency. Tests 18 and 19 show 100% reduction of recycled NO_X . At this condition, the methane to NO_X mole ratio was only 3.9. Other hydrocarbons or reducing gases could also be good candidates as doping reagents for in-furnace NO_X reduction.

<u>System Material Balance for In-Furnace Decomposition of Recycled Nitrogen Oxides</u>

Figure 5 shows a schematic diagram of a regenerable NO_X control process in which the NO_X is reinjected into the coal combustor for in-furnace disposal. A number of regenerable NO_X control processes now under development employ this approach. In the combustor, "a" mol/h of NO_X is being produced and is partially removed downstream by the sorbent within the reactor (absorber). The remaining NO_X , (100 – E₁)a/100 mol/h, is emitted into the atmosphere. The NO_X absorbed in the absorber reactor is separated from the sorbent through a regeneration process and is then recycled back to the combustor for in-furnace disposal.

Ĺ

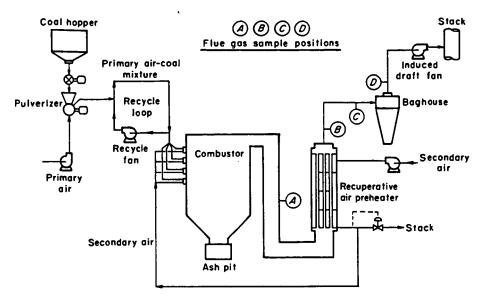


FIGURE 3. SIMPLIFIED FLOWSHEET OF 227 kg/h PULVERIZED-COAL-FIRED FURNACE.

L-81017

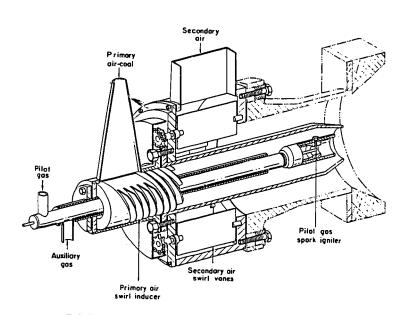


FIGURE 4. MULTI-FUEL BURNER ASSEMBLY.

479

If the in-furnace NO_{X} decomposition efficiency is not 100%, it would be desirable to determine if the NO_{X} concentration at the outlet of the combustor would reach steady state when the in-furnace NO_{X} disposal concept is applied to the overall operation.

At steady state, a material balance around the absorber may be defined as follows:

$$a + \left[\frac{(100 - c)x}{100}\right] = \left[\frac{(100 - E)a}{100}\right] + x \tag{4}$$

Therefore,

$$x = aE_1/c \tag{5}$$

Here, E2 is defined as the absorber $NO_{\rm X}$ removal efficiency relative to the net mass flow of $NO_{\rm X}$ entering the absorber.

$$E_2 = 100x/(a + [\frac{(100 - c)x}{100}])$$
 (6)

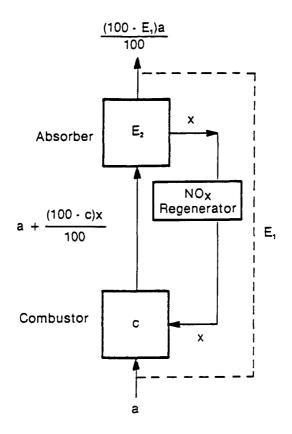
Equations (4) and (6) indicate that the NO_X recycle system will reach a steady state of NO_X concentration at each stage of the system. For example, given a = 100 mol/h, c = 70%, and E_1 = 90%, the steady-state recycle rate x can be found. From Equation (5), x = 128.6 mol/h of NO_X . This implies that if the absorber is designed for steady-state 90% NO_X removal from the flue gas produced from the combustor in a recycle mode, the NO_X removal capacity of this reactor (absorber) must be 128.6 mol/h of NO_X .

Low-NOx Burner and NOx Recycle Combination Process Scheme

Other possibilities also exist to reduce recycled NO $_{\rm X}$. One technique couples a low-NO $_{\rm X}$ burner and in-furnace NO $_{\rm X}$ reduction without the use of hydrocarbon doping (see Figure 5). The low-NO $_{\rm X}$ burner first reduces the NO $_{\rm X}$ produced from the combustor, thus reducing the burden on the absorber; this is then followed by the recycle of the regenerated NO $_{\rm X}$ for in-furnace reduction.

An example of this technique is demonstrated as follows (refer to Figure 5 and the previous sample calculations): Given a = 73 mol/h $NO_{\rm X}$ (assuming a low-NO $_{\rm X}$ burner with 27% $NO_{\rm X}$ reducing efficiency is in place), c=70% (percent of in-furnace reduction of recycled $NO_{\rm X}$), and the NO $_{\rm X}$ emission control is 90% removal of the NO $_{\rm X}$ produced in the combustor before the use of a low-NO $_{\rm X}$ burner, determine if the combined NO $_{\rm X}$ reduction through the coupling of low-NO $_{\rm X}$ burner and in-furnace reduction of recycled NO $_{\rm X}$ can meet the 90% NO $_{\rm X}$ reduction requirement.

The answer may best be illustrated in a tabulated form (see Table 3) by comparing overall $NO_{\rm x}$ removal efficiencies at various $NO_{\rm x}$ recycle rates.



a = NO_X produced in the combustor, mol/h

E, = system NO_X removal efficiency, in relation to "a", %

 E_2 = absorber NO_X removal (with NO_X recycle) efficiency, in relation to "a + (100 · c)x/100", %

c = destruction efficiency of recycled NO_X in the combustor, %

 $x = flow of NO_X$ recycled to combustor, mol/hr

FIGURE 5. SCHEMATIC DIAGRAM OF NITROGEN OXIDE RECYCLE.

Table 3. Combined NO_X Reduction Scheme

×	a + (100-c)x/100	(100-E ₁)a/100	E ₁
NO_X absorbed and then recycled, mol/h	NO _x entering absorber, mol/h	NO _x exiting absorber to stack, mol/h	Overall efficiency,
60	91	31	69
70	94	24	76
80	97	17	83
90	100	10	90

The calculated results show that given a low-NO $_{\rm X}$ burner with 27% NO $_{\rm X}$ reduction efficiency combined with in-furnace reduction of recycled NO $_{\rm X}$ at 70% efficiency, 90% overall NO $_{\rm X}$ reduction could be maintained.

CONCLUSIONS

The location of injection of recycled NO_X into the combustor is important. A high degree of mixing between the recycled NO_X and the entire body of oxidizer and/or combustion gas should be avoided. Doping the recycled NO_X stream with methane is very effective in destroying the injected NO_X . It is kinetically advantageous to keep the NO_X in a concentrated form when it comes in contact with the reducing gas. It appears that this approach generates a locally fuel-rich zone, minimizes the oxidation of methane, and probably creates a pool of hydrocarbon radicals that contribute to the destruction of NO_X .

Recirculation of NO $_{\rm X}$ to the combustor after the regeneration step, plus th use of either hydrocarbon doping or a low-NO $_{\rm X}$ burner, can destruct most or all the recycled NO $_{\rm X}$. These techniques should contribute to the development of cost-effective systems in which greater than 90% NO $_{\rm X}$ removal efficiencies can be obtained.

DISCLAIMER

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

 Mulholland, J.A.; Lanier, W.S. Application of Reburning for NO_X Control to a Firetube Package Boiler, Journal of Engineering for Gas Turbines and Power, Vol. 107, p. 739, July 1985.

i

- 2. McCarthy, J.M.; Chen, S.L.; Seeker, W.R.; Pershing, D.W. Pilot Scale Studies on the Application of Reburning for NO_X Control, presented at the Joint Symposium on Stationary Combustion NO_X Control, New Orleans, La., March 1987.
- Yeh, J.T.; Drummond, C.J.; Haslbeck, J.L.; Neal, L.G. The NOXSO Process: Simultaneous Removal of SO₂ and NO_X from Flue Gas, presented at the AIChE 1987 Spring National Meeting, Houston, Texas, March 29 -April 2, 1987.
- Wendt, J.O.L.; Sterling, C.V.; Matovich, M.A. Reduction of Sulfur Trioxide and Nitrogen Oxides by Secondary Fuel Injection, 14th Symposium (International) on Combustion, The Combustion Institute, 1973, p. 807
- 5. Chen, S.L.; Clark, W.C.; Heap, M.P.; Pershing, D.W.; Seeker, W.R. NO_X Reduction by Reburning With Gas and Coal: Bench Scale Studies, Proceedings of the 1982 Joint Symposium on Stationary Combustion NO_X Control, Vol. 1, Utility Boiler Applications. EPRI Report No. CS-3182, July 1983.